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MEMORANDUM

TO: John Ryan

MEMO NO.: D236-120

FROM: Gary Wilson

FILE:

SUBJECT: Addendum to September 17, 1984 Critique of Analytical Results For PAH-BNRR

DATE: September 28, 1984

In my critique of the recent PAH work for BNRR I discussed problem areas associated with part per trillion PAH work. At that time I discussed the inherent variability of trace organic measurements. Although I had some recovery data in Table I of that memo, it was not complete. This memo furnishes the hard numbers for all of the PAH work we have done to date and helps define the reliability of individual sample measurements. This data is built upon a larger data base than that in the previous table and is therefore the "final" evaluation. As such it is being used in the defining of the Q/C guidelines for future work.

Duplicates

Duplicates should measure the precision of the analysis. Field duplicates, such as used during the BNRR work, measure this precision taking into account sampling, storage, transport, extraction and analytical measurement. The statistical approach selected to analyze the duplicate data is one used by the EPA at Love Canal as a measure of intralaboratory precision. A discussion of the approach is attached as Attachment A.

In order to make the data more meaningful and to take into account the wide variability in concentrations encountered with "real" samples, we have used percent difference in place of difference in the equations.

$$di = \frac{(yi - xi)}{(yi + xi)/2} \times 100$$

As can be seen from the approach discussion, it is possible to predict the standard deviation to be applied to individual samples and to set up a 95% probability limit. This should give an indication of the likely variability for each sample measurement for each compound. By using percent, it makes it easier to understand what the 95% probability limit means. The 95% probability limit says that if a given sample were analyzed in replicate 95% of the replicates would fall within a range defined by the value measured plus or minus the 95% probability limit.

I have talked with EPA people as well as statisticians to determine the legitimacy of using percent difference in place of difference. Difference fails if the range of values exceeds an order of magnitude. The current data set of duplicates is not large enough to check the validity of substituting percent difference. However, the consensus is that the errors involved are not significant if the probability limits are used as estimates. There is no published data available and no other statistical scheme has been found, which would offer a better estimate.

The calculated 95% probability limits for percent difference for the low level PAH work are:

Naphthalene	$\pm$ 67%
Acenaphthylene	$\pm$ 31%
Acenaphthene	$\pm$ 36%
Fluorene	$\pm$ 21%
Phenanthrene/anthracene	$\pm$ 16%
Fluoranthene	$\pm$ 54%
Pyrene	$\pm$ 38%
Benz(a)Anthracene/Chrysene	$\pm$ 53%

Benzofluoranthenes	± 34%
Benzo(a)pyrene	± 42%

Spike Recovery

Analysis of distilled water spikes yields an overall measure of method accuracy. Throughout the PAH work performed over the past eighteen months, ERT has analyzed spikes. This data has been statistically analyzed with the following results:

	Recovery Mean	Standard Deviation
Naphthalene	54%	18%
Acenaphthylene	61%	28%
Acenaphthene	84%	19%
Phenanthrene	43%	22%
Fluoranthene	112%	28%
Pyrene	110%	19%
Chrysene	66%	23%
Benzofluoranthene	125%	35%
Benzo(a)pyrene	65%	29%
Dibenzo(ah)anthracene	31%	11%
Benzo(ghi)perylene	32%	15%

The above data does not include four recovery values for benzofluoranthene, benzo(a)pyrene, naphthalene. As discussed in the previous memo, we have had interference problems in the latest data sets. The four values are for recoveries performed during this period. The addition of these values to the data set yields the following results:

	Recovery Mean	Standard Deviation
Naphthalene	90%	76%
Benzofluoranthene	165%	66%
Benzo(a)pyrene	84%	49%

These values are a more realistic measure of the variability for the latest data for these compounds. For purposes of the development of the quality control guidelines we are using the tighter values shown by the data with the latest recovery for these compounds removed. Removal is justified under outlier statistics and makes sense considering that we know a special problem occurred in the latest data.

Surrogates

Surrogates are deuterated PAH added to every sample to measure method efficiency. They offer the best method of determining method efficiency because each sample has a surrogate recovery. I have analyzed all of the surrogate recovery data for the past eighteen months of PAH work. The results are as follows:

	Recovery Mean	Standard Deviation	95% Conf. Limits
Chrysene-d12	57%	31%	BDL-118%
Fluorene-d10	81%	34%	14-150%
Naphthalene-d8	88%	23%	43-133%

The final data reports for this summers BNRR work and all future reports will have these confidence limits included as well as indication of samples which fall outside the 95% confidence limits for surrogates. Table I gives a concise summary of the Q/C data presented herein.

Table I: Summary of PAH QC Data

Compound	Recovery Mean %	Recovery Std.Dev. %	95% Conf. Limit %	95% Probability Limit % *
Naphthalene	54	18	19-89	± 67
Acenaphthylene	61	28	6-116	± 31
Acenaphthene	84	19	47-121	± 36
Fluorene	-	-		± 21
Phenanthrene/ Anthracene	43	22	BDL-86	± 16
Fluoranthene	112	28	57-167	± 54
Pyrene	110	19	73-147	± 38
Benz(a)anthracene/ Chrysene	66	23	21-111	± 53
Benzofluoranthene	125	35	56-194	± 34
Benzo(a)pyrene	65	29	8-122	± 42
Dibenz(ah)anthracene	31	11	10-53	-
Benzo(ghi)perylene	32	15	3-61	-
Chrysene-d12	57	31	BDL-118	-
Fluorene-d10	81	34	14-150	-
Naphthalene-d8	88	23	43-133	-

* Takes into account sampling as well as analysis.

Appendix A

8.7 PRECISION AND ACCURACY EQUATIONS

The precision of analytical results on duplicate or triplicate collected samples shows the variability present in the measurement system; the accuracy of analytical results on known value QC samples shows the bias present in the analytical measurement. The equations used to estimate precision and accuracy are given in the following sections.

8.7.1 Intralaboratory Precision Equations

Intralaboratory measurement precision for each subcontractor laboratory will be estimated from its analysis of duplicate collected samples. For each duplicate sample we assume that the following mathematical model holds:

Y_i and X_i are independent, normally distributed variables both with mean μ_i and standard deviation σ. We assume the mean μ_i can change from day to day but σ is constant.

The intralaboratory precision is quantified by σ and it is estimated by computing the standard deviation of the differences divided by $\sqrt{2}$. The following equations are used:

Difference Between Duplicates

$$d_i = Y_i - X_i \tag{1}$$

where Y_i = concentration measured by duplicate 1,

X_i = concentration measured by duplicate 2 and

d_i = difference between duplicate analyses.

$$\bar{D} = \frac{1}{k} \sum_{i=1}^{k} d_i \tag{2}$$

where $\bar{D}$ = mean difference

k = number of duplicates

Standard Deviation of Differences (S_d)

$$S_d = \sqrt{\frac{1}{(k-1)} \left[\sum_{i=1}^{k} d_i^2 - \frac{1}{k} \left(\sum_{i=1}^{k} d_i \right)^2 \right]} \tag{3}$$

Estimate of the standard deviation of a single y or x value (S_y, S_x)

For a single y or x value the estimate of the standard deviation is $\frac{S_d}{\sqrt{2}}$

95% Probability Limits for a Single y or x Value

$$\text{Upper 95\% Probability Limits} = y \text{ or } x + 1.96 \frac{S_d}{\sqrt{2}} \quad (4)$$

$$\text{Lower 95\% Probability Limits} = y \text{ or } x - 1.96 \frac{S_d}{\sqrt{2}} \quad (5)$$

Intralaboratory Precision Reporting

For each set of duplicates analyzed, the following will be reported classified by pollutant, media analyzed and analytical laboratory:

y values, x values, differences

$\overline{D}$, mean difference

$\frac{S_d}{\sqrt{2}}$, standard deviation of a single value

$\pm 1.96 \frac{S_d}{\sqrt{2}}$, for Upper and Lower 95% Probability Limits

8.7.2 Interlaboratory Precision Equations

Interlaboratory measurement precision for each analytical subcontractor will be estimated from the analysis of duplicate or triplicate collected samples by the subcontractor and an EPA referee laboratory. As noted earlier in this section, air samples will be collected in duplicate and double quantities of biota samples will be prepared for analysis to provide duplicates for precision estimates. Water, soil and sediment samples will be collected in triplicate. The interlaboratory precision is quantified by the standard deviation of the difference between the subcontractor analysis results and the referee laboratory results. Somewhat different statistical treatment is required for duplicates and triplicates and is provided in the following subsections.